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## XXII.

## CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

# ON THE ACTION OF WATER UPON TRIBROMTRINITROBENZOL AND TRIBROMDINITROBENZOL.*

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Presented June 15, 1892.

In an article † recently published, C. A. Lobry de Bruyn describes the action of an aqueous solution of sodic carbonate upon the unsymmetrical trinitrobenzol (1, 2, 4) which produces the dinitrophenol (OH, 1, 2, 4) by the replacement of a nitro group by hydroxyl. After we had shown in an earlier paper ‡ that the nitro groups can be removed from tribromtrinitrobenzol by sodic alcoholates, M. Lobry de Bruyn suggested to us in the most courteous way that it would be interesting to see whether an aqueous solution of sodic carbonate would not have a similar effect on this substance, which seemed not improbable after his work already cited. The following paper contains an account of the work we undertook in accordance with this suggestion, the results of which can be briefly summarized as follows. Symmetrical tribromtrinitrobenzol (melting point 285°) is converted by boiling with sodic carbonate and water into a mixture of the sodium salts of trinitrophloroglucine and a tribromdinitrophenol, $C_6Br_3(NO_2)_2OH$, melting at 194°, which, so far as we can find, has not been described as yet. Tribromdinitrobenzol (melting point 192°, made from symmetrical tribrombenzol) gave under the same conditions a dibromdinitrophenol which melts at 147–148°, a melting point almost identical with that of the only other dibromdinitrophenol known (146°–146°.5), recently made by Garzino* by the action of nitric acid on the propionic ester of metabromphenol. This coincidence is, however, purely accidental, as in Garzino's phenol the bromine atoms stand in the ortho and para, in ours in the meta positions, to the hydroxyl. As was to be expected, the two phenols gave different salts, the potassium salt made by Garzino, containing one half of a molecule of water, while ours is anhydrous, his barium salt containing three, ours two molecules of water. Mixed with the dibromdinitrophenol is an oily phenol, which we have not succeeded in purifying in spite of many attempts.

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* The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy, by W. H. Warren.

† Rec. Trav. Chem., IX. 185.

‡ These Proceedings, XXV. 164.

The two substances, therefore, act with water and sodic carbonate in the same general manner as with sodic ethylate, the trinitro compound in both cases showing two parallel reactions, in one of which nitro groups, in the other bromine atoms, are removed, while the dinitro compound in both cases loses part of its bromine. It is to be observed, however, that while the alcoholate removes two nitro groups from the trinitro and two bromine atoms from the dinitro compound, water in each of these cases removes only one; although, like the alcoholates, it removes all three of the bromine atoms from the tribromtrinitrobenzol.

The constitution of the new tribromdinitrophenol can be only $C_6OHBrNO_2BrNO_2Br$, as the substance from which it is derived is symmetrical. The dibromdinitrophenol, on the other hand, can be either $C_6OHNO_2BrNO_2BrH$ or $C_6OHNO_2BrHBrNO_2$, and we have no experimental data for determining which of these two formulas is correct.

### *Action of Water and Sodic Carbonate on Tribromtrinitrobenzol.*

As this action takes place very slowly it is better to carry it on as follows. Four or more flasks provided with return condensers were charged each with about 1 gr. of tribromtrinitrobenzol and a moderate quantity of a dilute solution of sodic carbonate, and allowed to boil for twelve or more hours. After a short time the solution turned yellow, and at the end of the boiling had become deep red. The unaltered tribromtrinitrobenzol was filtered out, and boiled again with a fresh solution of sodic carbonate. The deep red filtrate showed the presence of sodic bromide and sodic nitrite when the proper tests were applied. When acidified with dilute sulphuric acid it turned from red to yellow, and a white precipitate was thrown down, to which we first turned our attention.

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* Att. R. Acc. Sc. Torino, XXV. 263. Ber. d. ch. Ges., 1892, R. 119.

The white product of the reaction, which is insoluble in water, was purified by dissolving it in ammonic hydrate, precipitating the barium salt from this solution by means of baric chloride, and treating the precipitate with alcohol, in which the barium salt of this substance is soluble. The filtered alcoholic solution was evaporated to dryness, the residue recrystallized several times from hot water, and then converted back into the free phenol by treatment with dilute hydrochloric acid. The free phenol was next dissolved in as little hot alcohol as possible, diluted with water till a precipitate began to form, which was then redissolved by the addition of a drop or two of alcohol, when upon cooling the substance separated in good crystals. This rather long method of purification can be replaced by simple crystallization of the free phenol from alcohol and water in the way just described, but, if an absolutely pure product is needed, the whole method described above should be used. After it showed the constant melting point 194°, it was dried at 100° and analyzed with the following results: —

I. 0.1951 gr. of the substance gave 12 c.c. of nitrogen at a temperature of 23° and a pressure of 768.1 mm.

II. 0.2089 gr. of the substance gave according to the method of Carius 0.2787 gr. of argentic bromide.

| | Calculated for $C_6Br_3(NO_2)_2OH$. | Found. I. | Found. II. |
|---|---|---|---|
| Nitrogen | 6.65 | 7.00 | |
| Bromine | 57.01 | | 56.76 |

These analyses show that the substance is a tribromdinitrophenol, and as it must have been formed from the tribromtrinitrobenzol by replacing one of the nitro groups by hydroxyl its constitution must be represented by the formula $C_6OHBrNO_2BrNO_2Br$. It is, so far as we are aware, the first tribromdinitrophenol which has been made.

To confirm the results of the preceding analyses the sodium salt was made by treating an excess of the phenol with pure sodic hydrate, filtering, and crystallizing from hot water, when it separated in long filiform yellow needles.

0.3076 gr. of this sodium salt gave 0.0504 gr. of sodic sulphate.

| | Calculated for $C_6Br_3(NO_2)_2ONa$. | Found |
|---|---|---|
| Sodium | 5.19 | 5.31 |

The sodium salt is soluble in ethyl or methyl alcohol even in the cold, and crystallizes from its alcoholic solution in long, flat, pointed needles.

*Properties of Tribromdinitrophenol.* — This substance crystallizes from dilute alcohol in square-ended needles usually grouped in arborescent or fan-shaped clusters looking like certain seaweeds; its color is white with a very faint shade of yellow. It melts at 194°, and is freely soluble in cold ethyl or methyl alcohol, or in ether, acetone, or glacial acetic acid; somewhat less soluble in benzol or chloroform, although still freely soluble in these liquids; soluble in carbonic disulphide; slightly in ligroine; very slightly in cold water, somewhat more soluble in hot. Dilute alcohol is the best solvent for obtaining crystals. Its alcoholic solution is distinctly yellow. The three strong acids have no apparent action on it. With alkalies it forms colored salts. A solution of the sodium salt gave precipitates consisting of yellow needles with salts of zinc, nickel, manganese, cobalt, chromium, cadmium, or lead. Cupric salts gave light green needles. In order to characterize the substance still further, its barium salt was prepared and analyzed.

*Baric Tribromdinitrophenylate,* $[C_6Br_3(NO_2)_2O]_2Ba$.—This substance was made by adding baric chloride to a concentrated solution of the ammonium or sodium salt, collecting the precipitate, and recrystallizing it several times from hot water. The salt contained no water of crystallization.

I. 0.6621 gr. of the salt gave 0.1545 gr. of baric sulphate.
II. 0.5066 gr. of the salt gave 0.1182 gr. of baric sulphate.

| | Calculated for $[C_6Br_3(NO_2)_2O]_2Ba$. | Found. | |
|---|---|---|---|
| | | I. | II. |
| Barium | 14.03 | 13.72 | 13.72 |

The baric tribromdinitrophenylate crystallizes from hot water in long yellow needles arranged in radiating circular groups. It is slightly soluble in cold water, more soluble in hot; freely in cold ethyl or methyl alcohol.

After the tribromdinitrophenol obtained by the acidification of the products of the reaction of water and sodic carbonate on tribrominitrobenzol had been filtered out, the filtrate was extracted with ether to obtain the organic substance, whose presence was indicated by its yellow color. The extract thus obtained melted over 190°, and contained bromine, indicating the probable presence of some tribromdinitrophenol. Upon boiling it with an aqueous solution of potassic carbonate, and allowing the solution to cool, small orange needles were obtained, which on acidification yielded the tribromdinitrophenol reoognized by its crystalline form and melting point. The highly colored filtrate from these crystals was now treated with dilute sulphuric acid, extracted with ether, and the extract crystallized from water by slow evaporation, when the characteristic hexagonal prisms of trinitrophloroglucine were obtained. As they showed a somewhat low melting point, 163–164°, instead of 167°, (see the preceding paper,) the original substance and its barium salt were analyzed with the following results: —

0.2130 gr. of the substance gave 30.3 c.c. of nitrogen at a temperature of 19°.5 and a pressure of 776.1 mm.

| | Calculated for $C_6(OH)_3(NO_2)_3$ | Found. |
|---|---|---|
| Nitrogen | 16.09 | 16.67 |

0.7080 gr. of the barium salt gave 0.5409 gr. of baric sulphate.

| | Calculated for $[C_6O_3(NO_2)_3]_2Ba_3$. | Found. |
|---|---|---|
| Barium | 44.33 | 44.91 |

The barium salt contained no water of crystallization. These analyses leave no doubt that the substance is trinitrophloroglucine, and the behavior of tribromtrinitrobenzol with water is therefore represented by the following reactions: —

$$C_6Br_3(NO_2)_3 + 3\,H_2O = C_6(OH)_3(NO_2)_3 + 3\,HBr.$$
$$C_6Br_3(NO_2)_3 + H_2O = C_6Br_3(NO_2)_2OH + HNO_2.$$

The action of sodic hydrate and water upon tribromtrinitrobenzol was similar to that of sodic carbonate and water, the products being trinitrophloroglucine and tribromdinitrophenol. The action in this case takes place somewhat more quickly than with the carbonate, but we preferred to use sodic carbonate in order to avoid the action of the boiling hydrate upon the glass of the flask. In the cold, sodic hydrate seemed to have no action on tribromtrinitrobenzol, which surprised us because Lobry de Bruyn* has found that it acts in the cold on the unsymmetrical trinitrobenzol.

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* Rec. Trav. Chem., IX. 193.

### *Action of Tribromdinitrobenzol with Water and Sodic Carbonate.*

Tribromdinitrobenzol (melting point 192°, made from symmetrical tribrombenzol) was boiled with an aqueous solution of sodic carbonate in the way just described for the trinitro compound. The action in this case was so slow that it was found better to continue the boiling for at least twenty-four hours before filtering. As in the preceding case, the color of the solution gradually became yellow, and later changed to red. After filtering out the unaltered tribromdinitrobenzol, the red filtrate, which contained sodic bromide and sodic nitrite, was acidified with dilute sulphuric acid, which turned it light yellow, and produced a cloudy precipitate, which after a long time collected on the bottom in the form of oil-drops. These were removed, the clear liquid extracted with ether, and the extract, which was small in amount and oily, added to the oil which had separated. This was then dissolved in ammonic hydrate and treated with baric chloride, when a precipitate was formed in a dark red solution.

The insoluble barium salt was decomposed with hydrochloric acid, and the phenol thus set free crystallized from dilute alcohol until it showed the constant melting point 147–148°, when it was dried at 100°, and analyzed with the following results: —

I. 0.1626 gr. of the substance gave by the method of Carius 0.1804 gr. of argentic bromide.

II. 0.2053 gr. of the substance gave 15.7 c.c. of nitrogen at a temperature of 26° and a pressure of 759.9 mm.

| | Calculated for $C_6HBr_2OH(NO_2)_2$. | Found. | |
|---|---|---|---|
| | | I. | II. |
| Bromine | 46.78 | 47.22 | |
| Nitrogen | 8.19 | | 8.49 |

These results prove that the substance is a dibromdinitrophenol formed by the replacement of one atom of bromine by one of hydroxyl, and as it is made from a symmetrical tribrom compound it must be isomeric with the one melting at 146°–146°.5 made by Garzino from metadibromphenol.

*Properties of Dibromdinitrophenol.* — This substance crystallizes from a hot alcoholic solution diluted with water until the substance begins to precipitate in thick yellow needles with square ends, arranged in radiating groups, although occasionally forms with two comb edges were observed. If crystallized from alcohol alone, in addition to the thick needles or prisms, other rather broad prismatic forms are observed, which have a notch in each end so that they resemble reels, or, when this formation is carried farther so that the notch has a flat bottom, crystals resembling spools are produced. Both these latter forms are very characteristic. It melts at 147–148°; and is very freely soluble in ethyl or methyl alcohol even in the cold, in ether, acetone, or glacial acetic acid; freely soluble in benzol or chloroform; soluble in carbonic disulphide; nearly insoluble in ligroine; water dissolves it to a certain extent when cold, still more, although not freely, when hot. The three strong acids have no apparent action on it. Alkalies form yellow salts with it.

*Potassic Dibromdinitrophenylate,* $C_6HBr_2OK(NO_2)_2$. — This salt was prepared by heating the free phenol with an aqueous solution of potassic carbonate, and was purified by crystallization from hot water. The salt was found to be free from water of crystallization. 0.1806 gr. of the air-dried salt lost only 0.0005 gr. at 120°. Garzino found one half of one molecule of water in his potassic dibromdinitrophenylate. The salt dried at 120° gave the following result on analysis: —

0.1664 gr. of the salt gave 0.0390 gr. of potassic sulphate.

| | Calculated for $C_6HBr_2OK(NO_2)_2$ | Found. |
|---|---|---|
| Potassium | 10.29 | 10.52 |

The salt crystallizes from hot water in arborescent clusters of orange-yellow needles, which are somewhat soluble in alcohol, but not freely even when it is hot.

*Baric Dibromdinitrophenylate,* $[C_6HBr_2O(NO_2)_2]_2Ba2H_2O$.—The salt was made by boiling the phenol with water and baric carbonate, and purified by crystallization from boiling water, when it was analyzed with the following results: —

I. 0.2834 gr. of the salt dried in the air lost 0.0116 gr. at 120°.
II. 0.2834 gr. of the air-dried salt lost 0.0135 gr. at 120°.
III. 0.2831 gr. of the air-dried salt lost 0.0121 gr. at 120°.

| | Calculated for $[C_6HBr_2O(NO_2)_2]_2Ba2H_2O$. | Found. | | |
|---|---|---|---|---|
| | | I | II | III. |
| Water | 4.21 | 4.09 | 4.76 | 4.27 |

Three molecules of water of crystallization, the amount found by Garzino in his barium salt, would give 6.19 per cent of water.

IV. 0.3923 gr. of the salt dried at 120° gave 0.1112 gr. of baric sulphate.

V. 0.2668 gr. of the salt dried at 120° gave 0.0754 gr. of baric sulphate.

| | Calculated for $[C_6HBr_2O(NO_2)_2]_2Ba$. | Found. | |
|---|---|---|---|
| | | IV. | V. |
| Barium | 16.73 | 16.66 | 16.62 |

The salt is yellow while it contains its water of crystallization, but turns orange as it loses it, and this change takes place in a desiccator over sulphuric acid, as under these circumstances it loses all but an insignificant fraction of the water which it contains. The dried salt absorbs water very eagerly from the air, turning from orange to yellow again. It crystallizes from boiling water in clusters of radiating needles, and is soluble in alcohol.

The dark red filtrate from the precipitate of the barium salt of dibromdinitrophenol gave upon acidification an oily precipitate, which has resisted all our efforts to bring it into a state fit for analysis; it is probable that this could be done by often repeated fractional precipitation, but we do not think the identification of the substance of sufficient importance to justify the large expenditure of time and work necessary to provide material enough for this purpose. Several analyses, which we made to determine the purity of our preparations, seemed to point to the presence of a substance having the composition $C_6HBr_2NO_2(OH)_2$, but, as at the same time they proved that our products were decidedly impure, no weight should be given to this indication, although the formation of some such substance is to be expected from the appearance of sodic nitrite among the products of the reaction.

Sodic hydrate acts upon tribromdinitrobenzol in the same way that sodic carbonate does, but somewhat more rapidly. It has apparently no action in the cold.